

# The influence of the spray deposition parameters in the photovoltaic response of the three-dimensional (3D) solar cell: TCO/ dense TiO<sub>2</sub>/ CuSbS<sub>2</sub>/ graphite

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The paper presents the influence of spray deposition parameters, of CuSbS<sub>2</sub> thin films, in the photovoltaic response of the 3D solar cell: TCO/ dense TiO<sub>2</sub>/ CuSbS<sub>2</sub>/ graphite. The cell components, TiO<sub>2</sub> and CuSbS<sub>2</sub> thin films, were obtained via Spray Pyrolysis Deposition (SPD) technique. The spray height and the breaks between two depositions were varied for the CuSbS<sub>2</sub> thin films. XRD, AFM, UV-VIS Spectroscopy and current-voltage measurements were performed in order to identify the properties of the obtained films and cells.

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## 1. Introduction

The development of the three-dimensional (3D) solar cell using as absorber material CuSbS<sub>2</sub> represent an alternative to the 3D solar cells presented by M. Nanu in 2004, [1] and latter in 2006, [2] in which the absorber material is CuInS<sub>2</sub>. Even if the best efficiencies were reported for the cells made from TiO<sub>2</sub> (anatase) transparent n-type material and CuInS<sub>2</sub> absorber material, [1-3], due to the high price and the low resources of CuInS<sub>2</sub>, new alternatives to this material are searched. CuSbS<sub>2</sub> represent a new alternative having a direct band gap of around 1.5 eV and its properties match with the requirement for the photovoltaic materials, [4, 5]. Until this moment the deposition of CuSbS<sub>2</sub> thin films are reported in literature by annealing chemically deposited Sb<sub>2</sub>S<sub>3</sub>-CuS thin films [4], [6], solvothermal method, [7] and spray pyrolysis deposition, SPD (in the work of our group), [8].

In the development of an efficient 3D cell an important part is the n and p-type semiconductors interface. A good TiO<sub>2</sub>/CuSbS<sub>2</sub> interface leading to a good contact on large surfaces, avoids recombination and thus a good photovoltaic response. This can be obtained by tailoring the films structure, morphology and band gap a way to do this is represented by the variation of the deposition parameters. The previous researches proved that the precursor ratios and the deposition temperature represent a method to tailor the film properties, [8, 9].

The paper present the results obtained at the investigation of deposition parameters (spray height and the break between two depositions) of CuSbS<sub>2</sub> thin film (a determinant component in the development of an efficient 3D solar cell).

The influence of deposition parameters on the CuSbS<sub>2</sub> properties obtained by SPD is only at the beginning and not reported by another group of research. SPD represent a relative simple and low cost deposition method, suitable for

large area thin films deposition and tailoring of structural, morphological and electrical properties, [10, 11, 12].

## 2. Experimental

### 2.1. Deposition part

CuSbS<sub>2</sub> films are deposited on SnO<sub>2</sub>: F substrate (transparent conducting oxide, TCO, TEC 8/ 3mm) and TCO/ dense TiO<sub>2</sub> structure (100nm deposited by SPD at the deposition parameters presented in reference [10]) using as precursors copper(II)-chloride dehydrate, CuCl<sub>2</sub>·2H<sub>2</sub>O, antimony (III) acetate (CH<sub>3</sub>COO)<sub>3</sub>Sb, 99.99%, and thiourea H<sub>2</sub>NCSNH<sub>2</sub>, 99% (both, as sulphur source and as complexing agent) at the precursor weight ratio 1:2.57: 5.71 in aqueous solutions. Small amounts of HCl are used to increase the solubility of antimony acetate. In order to obtain CuSbS<sub>2</sub> films with the controlled structural and electrical properties, the deposition parameters: spray height (25 cm, 30 cm, and 35cm) and the break between two depositions (60 s and 90s) were varied.

During spraying, the deposition temperature and the pressure of the carrier gas (nitrogen) were fixed at 240°C and 1.2 bar.

### 2.2. Analysis part

The CuSbS<sub>2</sub> films deposited on TCO were analyzed using X-Ray Diffraction (XRD, Bruker D8 Advance Diffractometer), Atomic Force Microscopy (AFM, NT-MDT model BL222RNTE), in contact mod, with Si-tip (CSG10, force constant 0.15 N/m, tip radius 10 nm) and UV - VIS Spectroscopy (UV - VIS spectrophotometer Perkin Elmer Lambda 25 UV/VIS).

The 3D cells were analyzed by current-voltage (I-V) measurement recorded in dark and under illumination using an DC Source Meter, Keithley, model 2400 and an calibrated solar simulator SolarConstant 1200 (K.H. Steuernagel

Lichttechnik GmbH) as visible light source. Graphite paste (graphite conductive adhesive aqueous based, Alfa Aesar) is used for contacts.

### 3. Results and discussions

Precedent researches proves that the deposition parameters of the absorber material  $\text{CuSbS}_2$  as precursor weight ratios and deposition temperature can influence the structural and electrical properties of the material and the photovoltaic response of the 3D cell, [8, 9, 10]. The present research presents the investigations of deposition parameters: spray height and the break between two depositions as two important factors in the photovoltaic response of the TCO/dense  $\text{TiO}_2$  (anatase)/ $\text{CuSbS}_2$ /graphite cell.

The  $\text{CuSbS}_2$  thin films deposited on TCO at the varied parameters (presented in the experimental part) investigated by X-ray Diffraction reveal the formation of crystalline  $\text{CuSbS}_2$  thin films with orthorhombic structure in conformity with JCPDS: 44-1417, Fig. 1. The XRD patterns also show the formation of  $\text{Sb}_2\text{S}_3$  rich structures ( $2\theta = 25.801$  and orientation (111)) with an orthorhombic system in conformity with JCPDS: 74-1046. The presence of the  $\text{Sb}_2\text{S}_3$  can influence the properties of the  $\text{CuSbS}_2$  films and the photovoltaic response of the developed cells, things that will be investigated in the paper.

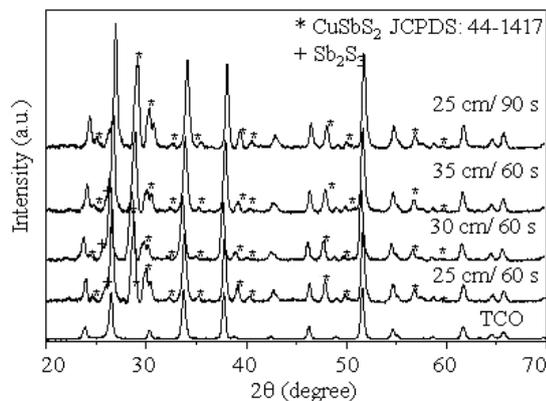


Fig. 1. XRD pattern of  $\text{CuSbS}_2$  thin films deposited on TCO at  $240^\circ\text{C}$  and the varied parameters.

The XRD patterns were used to identify the  $\text{CuSbS}_2$  thin films but also to calculate the crystallite size,  $D$ , formed in the films at the varied parameters. The crystallite sizes were calculated using Scherrer formula:

$$D = \frac{k\lambda}{\beta \cos\theta} = \frac{0.9\lambda}{\beta \cos\theta}, \quad (1)$$

where:  $\lambda$  – the wavelength ( $\lambda = 1.54060 \text{ \AA}$ ),  $k$  – shape coefficient (usually is 0.9),  $\beta$  – the full-width at half-maximum of the peak in radian, and  $\theta$  – the Bragg angle.

The used picks for the identification of  $D$  formed in the  $\text{CuSbS}_2$  thin films were at  $2\theta = 47.864$ , correspondent to the (002) orientation. The same peak is used to determine the

microstrains that are presented in obtained films using the next relation:

$$\varepsilon = \frac{\beta}{4\text{tg}\theta}, \quad (2)$$

The values are presented in Table 1 proving that the increasing of the deposition height and the breaks between two depositions leads to higher crystallite sizes due to the pyrolysis process that take place during the depositions at the both parameters. With the increasing of the deposition height the pyrolysis process is modified by changing the solvent evaporation and so the formation of the films. The time between two depositions is essential for the pyrolysis process but also for the dry process. A shorter time between two depositions prevent a complete pyrolysis process, a total remote of the solvent and of the secondary reaction products leading to the formation of an impurity films or can prevent the film formation. A longer time between two depositions leads to the formation of a stratification layer by layer from the wanted material, and not the formation of a homogeneous unit film.

These factors can determine:

1) the formation of a thinner films (values obtained from the absorption date and presented in Table 1) with grain size that increase with the distance for the first varied parameter. The microstrain that tack place between the crystals and calculated with the relation 2 present a decreasing in the values with the increase of the crystal size confirming the formation of an open porous structure with the enhancement of the sprayed distance as can be seen from the AFM images, Fig. 2a, b and c, and

2) the formation of the thicker films with the increasing of the breaks between the sprays, Table 2. Bigger crystallites are formed and the microstrain values calculated for the films prove the formation of a more open porous structure with the increasing of the breaks, proved also by the AFM images Fig. 2a and Fig. 2d. This can be a result of a stratified  $\text{CuSbS}_2$  thin films formation due to the higher breaks between the sprays.

Table 1. Crystallite size and microstrains presented in the  $\text{CuSbS}_2$  films deposited at the varied parameters.

H (cm)/ t(s)	(hkl)	D (nm)	$\varepsilon$ ( $10^{-4}$ )	G (nm)
25/ 60	002	41.62	20.55	277.56
30/ 60	002	41.96	20.37	212.17
35/ 60	002	42.18	20.27	206.34
25/ 90	002	43.25	19.76	285.03

An important role in the development of a functional solar cell is give by the values of the n and p type semiconductor band gaps and the aliniament of the band energies. If for the  $\text{TiO}_2$  (anatas) the value of the band gap is fixed for 3.22 eV (as is presented in literature for this films deposited by SPD, [13]) for the absorber  $\text{CuSbS}_2$

thin films the value of the  $E_g$  is presented in literature to be 1.52eV. This value is for the  $CuSbS_2$  thin films obtained by annealing of  $Sb_2S_3$ - $CuS$  thin films and not by SPD. The value of  $E_g$  for our films are obtained from absorption data reported at photon energy ( $h\nu$ , eV), Fig. 2, and the values are presented in Table 2. The obtained values (with an average of 1.02 eV) are lower than the literature value. The difference in the values can be related to the presence of  $Sb_2S_3$ . Future work in the research of the  $Sb_2S_3$  influence must be performed.

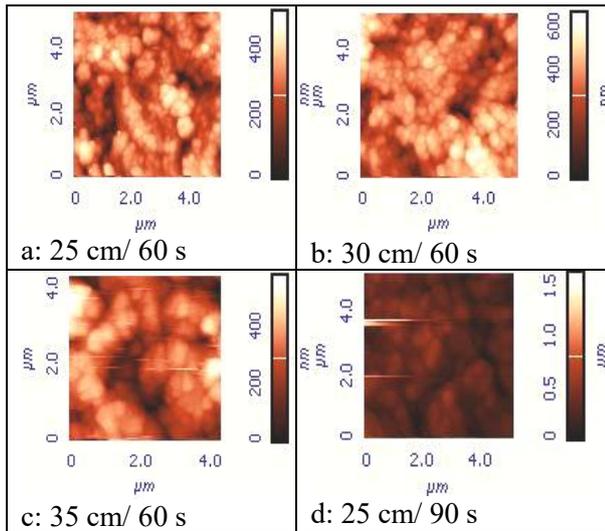


Fig. 2. AFM images of  $CuSbS_2$  thin films deposited on TCO at 240 °C and the varied parameters.

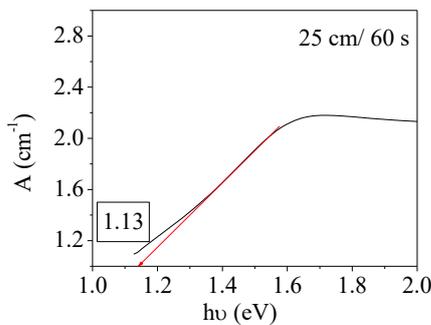


Fig. 3. Band gap value for  $CuSbS_2$  thin films deposited at 240 °C, 25 cm and 1.2 bar.

To identify the photovoltaic response of the developed cells, I-V curves were recorded in dark and under illumination. The best photovoltaic response was shown for the sample deposited at 240 °C, 25 cm and 60s,  $E_g = 1.13$  eV and having the cell characteristics  $V_{oc} = 90$  mV,  $I_{sc} = 2.39 \cdot 10^{-2}$  mA and  $FF = 0.286$ , Fig. 4. The photovoltaic responses of the developed cells are presented in Table 2.

The variation of the band gaps has proven its importance in the development of the working cell with the increasing of the spray distance:  $E_g$  smaller than 0.92 eV prevents a correct alignment of the  $TiO_2$  and  $CuSbS_2$  bands but at  $E_g$  larger than 1.13 eV the alignment of the band is obtained.

The absence of the photovoltaic response for the cell made with  $CuSbS_2$  deposited at 240°C, 25 cm height, 1.2 bar and 90 s can be a result of the stratified  $CuSbS_2$  film that can prevent a good transport of the carriers.

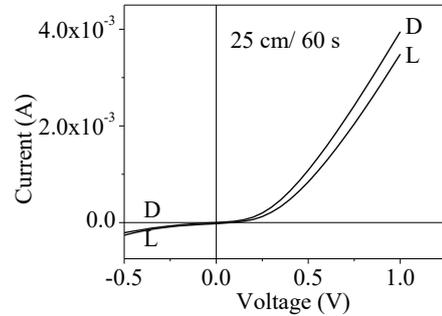


Fig. 4. I-V curves measured in dark and under illumination of TCO/ dense  $TiO_2$ /  $CuSbS_2$  (deposited at 240°C, 25 cm and 60s) / graphite cell.

Table 2. Cells parameters for the structures made with  $CuSbS_2$  thin films deposited at the varied parameters.

$H_{SPD}$ (cm)/ t (s)	25/ 60	30/ 60	35/ 60	25/ 90
$E_g$ (eV)	1.13	0.94	0.92	1.15
$V_{oc}$ (mV)	90	5	0	0
$I_{sc}$ (A)	$2.39 \cdot 10^{-5}$	$5.09 \cdot 10^{-6}$	0	0
$V_{max}$ (mV)	50	2.4	0	0
$I_{max}$ (A)	$1.23 \cdot 10^{-5}$	$2.52 \cdot 10^{-6}$	0	0
FF	0.286	0.237	0	0

In order to avoid the electron-hole pair recombination mentioned before, and to favor the alignment of the energy bands, the deposition, between these two layers, of a tunnel and a buffer layer, are recommended for the next researches.

#### 4. Conclusions

The research presented in this paper proves that the deposition parameters as: spray height and the break between two depositions of the  $CuSbS_2$  thin film (used as p-type absorber material) play an important role in  $CuSbS_2$  thin films properties and the photovoltaic response of the TCO/ dense  $TiO_2$ /  $CuSbS_2$ / graphite.

The photovoltaic response for the cells are lower and this can be a result of the Sb-rich films (the presence of  $Sb_2S_3$  in the films pattern), porous structure, band gaps values of the  $CuSbS_2$  thin films or the bad alignment of the energy bands.

For the next researches a control of the  $CuSbS_2$  thin film morphology, the Cu-rich  $CuSbS_2$  thin films and the deposition of tunnel or buffer layers between the  $TiO_2$  and  $CuSbS_2$  layers, must be investigated.

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### References

- [1] M. Nanu, J. Schoonman, A. Goossens, *Advanced Materials* **16**(5), 453-456 (2004).
- [2] Barbara van der Zanden, Camelia Joanta, Harry Donker, Marian Nanu, Ben Meester, 21st European Photovoltaic Solar Energy Conference and Exhibition, p. 267-269, ISBN 3-936338-20-5 (2006).
- [3] M. Nanu, 3D inorganic solid state solar cells, PhD theses, Delft, Netherlands, ISBN-10 : 90/9020553-5 (2006).
- [4] Y. Rodríguez Lazcano, M. T. S. Nair, P. K. Nair, *Journal of Crystal* **223**, 399-406 (2001).
- [5] J. Nelson, *The Physics of Solar Cells*, Imperial College Press, 2003.
- [6] Y. Rodríguez-Lazcano, M. T. S. Nair, P. K. Nair, *Journal of the Electrochemical Society* **152**, G635-G638 (2005).
- [7] Huilan Su, Yi Xie, Shoukang Wan, Bin Li, Yitai Qian, *Solid State Ionics* **123**, 319-324 (1999).
- [8] S. Manolache, A. Duta, L. Isac, Marian Nanu, Albert Goossens, Joop Schoonman, *Thin Solid Films* **515**, 5957 (2007).
- [9] S. Manolache, L. Andronic, A. Duta, presented at EMRS 2007 Conference.
- [10] S. Manolache, A. Andronic, A. Duta, A. Enesca, J. Optoelectron. *Adv. Mater.* **9**(5), 1269 (2007).
- [11] A., Duta, S. A., Manolache, M., Nanu, A., Goossens, J., Schoonman, *Thin Solid Films* **511-512**, 154 (2006).
- [12] Pramod S. Patil, *Materials Chemistry and Physics* **59**,185-198 (1999).
- [13] C. Zilverentant, *Hybrid Solar Cells of Titanium Dioxide Sensitized with Organic semiconductors*, 2003, Delft, Netherlands.

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